Photolysis of Diborane at 1849 Å*

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The photolysis of diborane at 1849 Å has been studied in a specially constructed, internal-type mercury-vapor lamp. The products have been found to be H_2, B_4H_{10}, B_5H_{11}, and, at low pressures, a —BH— polymer. Reaction orders at 4°C have been obtained from linear plots of reaction products vs time for a range of diborane pressures from 0.08 to 80 cm, and at two light intensities. Linear relations between products and time existed only at very low conversions (~1%), which required the development of a low-temperature separation method for manipulating and analyzing the traces of B_4H_{10} and B_5H_{11}. Because of the reactivity of these compounds, a detailed conditioning procedure was employed for the glass system.

A mechanism consistant with the kinetic data and suggested by the kinetic results of thermal and photosensitized decomposition of diborane is postulated: the B_5H_{11} is assumed to be formed from a dissociation of B_2H_6 into BH_3's, the latter arising from an excited molecule. The B_4H_{10} and polymer are assumed to be formed from a dissociation of B_2H_6 into B_2H_5 and H, followed by radical recombination. There is a significant difference between the kinetics of thermal and photochemical B_5H_{11} formation, a result which may be due to the considerable energy excess of the 1849 quantum over that needed for dissociation (~125-kcal excess). These kinetic results raise a number of interesting questions, questions which can only be resolved through further investigations of effects due to light intensity, added inert gases, and temperature.

The primary quantum yield of the step forming B_2H_5 and H is about 10 times higher than that of the one forming BH_3's. A rather rough estimate suggests that the former is of the order of magnitude of unity.

INTRODUCTION

ACKNOWLEDGE of the mechanism of the photochemical decomposition of diborane is of interest, partly because of the possible existence of elementary steps and intermediates which may be common to the known thermal and photosensitized decompositions of diborane. For instance, in the case of hydrocarbon-free radicals, photolysis has been one of the most useful tools for studying their reactions.

Many thermal studies have been made on diborane,[1–3] the initial products being B_5H_{11} and H_2, and on its reactions with such compounds as C_2H_4,[4] H_2O,[5] and D_2.[6,7] Common to these reactions is the dependence of the rate of formation of some product on a one-half or three-halves power of the diborane concentration. To account for this behavior, these authors postulate a dissociation of diborane into two BH_3 groups, followed by subsequent reaction of the BH_3's with diborane or with another reactant.[1–7] For example, for diborane thermal decomposition, a mechanism consistent with the kinetic data is[1–3]

$$B_2H_6 \rightleftharpoons 2BH_3,$$

$$BH_3 + B_2H_6 \rightarrow B_3H_9 \xrightarrow{B_2H_6} B_5H_{11} + 2H_2.$$

The mercury-photosensitized decomposition of diborane was investigated by Hirata and Gunning,[8] who found B_4H_{10} and H_2 to be the principal products. They postulated B_2H_5 as a short-lived intermediate, B–H ruptures being quite common in mercury photosensitizations:

$$B_2H_6 + Hg^* \rightarrow B_2H_5 + H + Hg,$$

$$2B_2H_5 \rightarrow B_4H_{10}.$$

The only reported study of the direct photolysis of diborane is that of Stock and Friederici[9] who qualitatively observed that irradiation of diborane by a quartz mercury-vapor lamp resulted in a pressure increase and in a formation of yellow-white crystals.

In the present study diborane was decomposed by its absorption of the 1849-Å line from a low-pressure mercury-vapor lamp. The products were identified to be B_4H_{10}, B_5H_{11}, H_2, and a polymer. The importance of restricting the investigation to unusually low-percent conversions was established (typically of the order of 1%) and initial rates were measured over a wide range of diborane pressures (0.08 to 80 cm) but, because of experimental limitations, only over a limited range of light intensities (factor of 6). The results and the postulated mechanism are presented below. The experimental procedures finally adopted are described in

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† Allied Chemical and Dye Company Fellow 1957–1958.

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[2] J. K. Bragg, L. V. McCarty, and F. J. Norton, J. Am. Chem. Soc. **73**, 2134 (1951).

[3] R. D. Stewart and R. G. Adler, talk given at American Chemical Society Meeting in September 1958.

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[6] P. C. Maybury and W. S. Koski, J. Chem. Phys. **21**, 742 (1953).

[7] R. A. Marcus, J. Am. Chem. Soc. **23**, 1107 (1955).

[8] T. Hirata and H. E. Gunning, J. Chem. Phys. **27**, 477 (1957).

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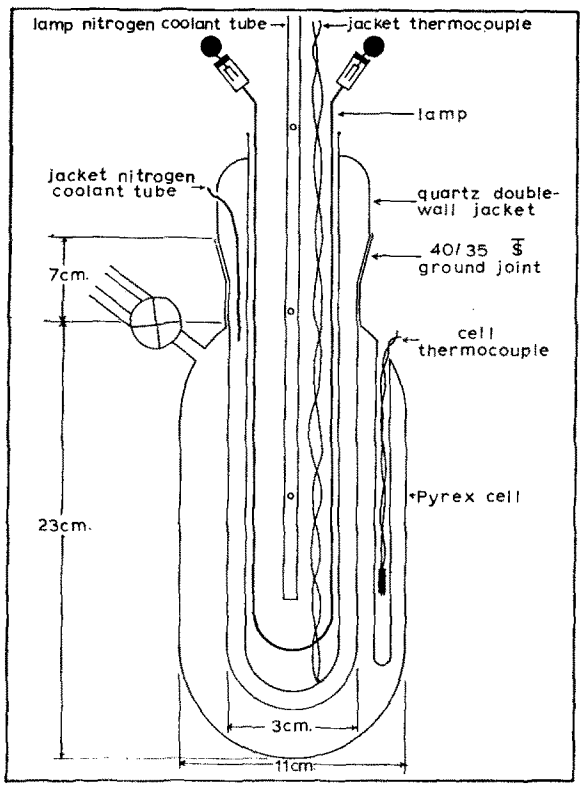

FIG. 1. Reaction cell, quartz jacket and mercury-vapor lamp. Cell volume is 1.55 liter.

detail. Many problems had to be overcome in order to maintain, transport, and analyze small quantities of B_4H_{10} and B_5H_{11}.

EXPERIMENTAL

Chemicals

Diborane (Olin Matheson) was stored in a 3-liter glass reservoir. To remove hydrogen and higher boranes, it was subjected to several cycles of freezing at −196°C, evacuation, melting, and refreezing until the pressure at −196°C was about 10^{-4} mm, and was then distilled from a bath of allyl chloride slush at −136°C to a trap at −196°C. This purified diborane was allowed to warm up and distill slowly, only the middle fraction being transferred to the reaction vessel. *Hydrogen*, *acetic acid*, and *allyl chloride* were Research Grade. Commercial Grade *ammonia* was purified by several trap-to-trap distillations from −78° to −196°C.

Apparatus

The low-pressure mercury vapor lamp[10] emitted a strong, monochromatic 1849 Å line, close to the 1820 Å absorption maximum[11] of gaseous diborane. Specially fabricated for this purpose by Hanovia from high-purity 0.5-mm wall quartz, it contained 10 mm of a 75% neon–25% argon mixture. Activated by a 3000 V GE luminous-tube transformer, it drew about 30 mA at 800 V.

The U-shaped lamp fitted in a quartz wall. The latter was set in a reaction vessel, as shown in Fig. 1. The well contained a double wall of 0.5-mm quartz which could be filled with appropriate liquid light filters. To minimize heating of the reaction vessel (and light absorption by atmospheric oxygen), precooled nitrogen was passed through the unfilled double wall and the lamp region, keeping the lamp at about 25°C. For the "high" light-intensity measurements, no liquid filter was used; for the low-intensity measurements, de-ionized water ($\sim 10^6\Omega$) was poured into the double wall just prior to the actual photolysis. By using this internal-type illumination, measurable amounts of products were formed in a time sufficiently short that no detectable opaque film formed upon the quartz. This problem was a serious difficulty in the past and in the earliest, long-time irradiations of this study.

The precise separation of the gaseous boron hydrides, after reaction, was performed in a LeRoy low-temperature fractional-condensation column.[12]

Connected to the reaction vessel were several U traps, a mercury diffusion pump, and a LeRoy column in parallel, a Toepler pump, and a gas buret. In the analysis, the hydrogen passed through the diffusion pump while the boranes passed through the LeRoy column. The buret (a 3-mm capillary column attached to an auxiliary bulb) could detect 0.01 μmole. It had a dead end instead of the conventional stopcock, to eliminate the observed solution of the hydrides under compression in stopcock grease.

The entire system was evacuated with a Welch Duo Seal pump and a two-stage mercury diffusion pump, separated from the reaction system by two −196°C traps to prevent passage of mercury vapor. To test qualitatively the effectiveness of the elimination of mercury vapor from the reaction vessel, a liquid-nitrogen trapping was made on a U trap in the reaction system before and after each photolysis. No trace of the characteristic black mercury ring was found.

The diborane pressure was measured with a U-shaped manometer (containing 703 silicone fluid), one arm of which was connected to the reaction vessel and the other, to the high-vacuum manifold. In the relatively fewer experiments employing pressures greater than 7 cm, an external helium pressure was applied to one arm and read on a mercury manometer. This mercury could not come into contact with the diborane.

High-pressure stopcocks were employed in the reaction vessel and manometer, and precision vacuum stopcocks in the analytical section. Apiezon "T" grease was used throughout. The pressures of the boron hydride products were kept very low by the low con-

[10] C. G. McDonald, A. Kahn and H. E. Gunning, J. Chem. Phys. **22**, 908 (1954).
[11] E. Blum and G. Herzberg, J. Phys. Chem. **41**, 91 (1937).
[12] D. J. LeRoy, Can. J. Research **B28**, 492 (1950).

version and the low separation temperature. There proved to be only small losses due to reaction with grease.[13]

As described in detail elsewhere[13] and discussed later, the U traps, the Toepler pump, and the gas buret were extensively conditioned, after any exposure to air, by passage of B_4H_{10} and B_5H_{11}, while the reaction cell was conditioned by a preliminary photolysis.

Photolysis Procedure

Prior to each photolysis and to prevent buildup of white polymer on the walls, the reaction vessel and quartz jacket were cleaned with hot, concentrated nitric-sulfuric acid and washed with water and with methyl alcohol. The reaction vessel was then evacuated for several hours at 70°C. The diborane was then purified and added to the reaction vessel, as described earlier. The cell was kept in a Dewar at 0°C.

A "cell-conditioning" photolysis was next performed, since early experiments of this study showed that even after the degassing of the cell at elevated temperatures, surface contaminants remained. They appeared in the hydrogen analysis and also reacted with small amounts of B_5H_{11}. Both these problems were eliminated, except for very small blanks, by this preliminary "cell-conditioning" photolysis of the measured-out diborane in the reaction cell. Appropriate irradiation times for conditioning proved to be 400, 400, 100, and zero sec for diborane pressures of 0.08, 0.25, 1.3, and 7 to 80 cm, respectively. These very short times were optimum since too long a conditioning reduced the absorbed light intensity through formation of an opaque film.[13]

This diborane sample was again purified in the manner described earlier. After the nitrogen coolant gas had begun flowing through the quartz jacket, the lamp was warmed up for twenty minutes, during which time the cell was evacuated. About three minutes before reaction, the diborane was allowed to expand from the liquid-nitrogen trap into a 500-cc "expansion bulb" kept at room temperature.

To initiate the reaction, a two-way stopcock through which the cell was being evacuated was rotated to connect the cell with the expansion bulb containing the gaseous diborane. The reaction time was not uncertain by more than one-half second. The reaction cell was then isolated from the expansion bulb to prevent loss of products. The reaction was terminated by extinguishing the lamp.

Analytical Procedure

Upon completion of the photolysis, the borane mixture was condensed in two consecutive U traps at −196°C. The noncondensed hydrogen was transferred through them into the gas buret via the mercury diffusion and Toepler pumps. The major portion of the diborane was next separated by two successive trap-to-trap distillations (−136° to −196°C). The remaining higher boranes and residual diborane were condensed in the LeRoy column at −196°C for the precision separation.[13] The residual diborane was removed from the column at −154°C and discarded. B_4H_{10} was next separated at −120°C and was collected in a trap at −196°C. The temperature of the column was then raised to −74°C and the evolved B_5H_{11} was collected in a second trap at −196°C. The separations were considered complete when a steady pressure of less than one-half micron had been achieved. The boranes were measured separately in the gas buret.

Results of tests described elsewhere,[13] in which known amounts of B_4H_{10} and B_5H_{11} were introduced, showed the effectiveness of the separation as well as that of the conditioning of the apparatus.

RESULTS

Product Identification

Besides the hydrogen, the main gaseous products were B_4H_{10} and B_5H_{11}. These were identified by collecting each fraction from the LeRoy column in an adsorption cell with NaCl windows and measuring its infrared-absorption spectra on a Perkin–Elmer model No. 21 spectrometer. The spectra were found to be the same as those reported for the pure compounds.[14] B_4H_{10} was identified mainly by comparing the observed ratio of the 4.05 to the 4.65-μ peaks with the reported ratio, while for B_5H_{11} the ratios of the 9.60 to the 4.87-μ peaks were compared. Other ir. spectral evidence amply supported these identifications.[13]

Direct identification of the "polymer" was not undertaken partly because of its nonvolatility and its small amount. The existence of a polymer was demonstrated by long, large conversion photolyses, in which a white deposit was visible on the inner quartz jacket and the Pyrex reaction cell. In addition, material balance from the hydrogen and the above two boranes could be obtained if a polymer was postulated. In early measurements involving large conversions, the H/B ratio in the polymer could be measured from an additional knowledge of the amount of diborane consumed, and it was found to be approximately 1.1. A ratio of unity was used in the subsequent calculations.

Temperature

Although the outer cylindrical surface of the reaction volume was at 0°C, the temperature of the inner surface, i.e. at the quartz jacket, was higher due to the lamp. With the lamp cooled as described earlier, the average temperature in the reaction vessel was measured by comparing the pressure of a nonreactive gas in the vessel in the dark with its pressure when il-

[13] W. C. Kreye, Ph.D. thesis, Polytechnic Institute of Brooklyn (1960).

[14] L. V. McCarty, G. S. Smith, and R. S. McDonald, Anal. Chem. **26**, 1027 (1954).

TABLE I. Reaction products at various times and pressure. Low light intensity.

Expt. No.	$P_{B_2H_6}$ (cm)	Irradiation time (sec)	Products (μmoles) H_2	B_4H_{10}	B_5H_{11}
248	0.079	150	0.34	0.04	0.02
251	0.081	400	1.10	0.11	0.09
247	0.082	600	1.95	0.15$_5$	0.17
252	0.250	50	0.44	0.08	0.05
221	0.251	220	1.73	0.25	0.26
219	0.251	600	4.67	0.57	0.76
228	1.28	200	6.67	1.49	1.12
227	1.29	600	18.2	4.48	3.22
155	7.10	200	11.6	5.39	1.72
136	7.12	300	17.4	8.03	2.83
154	7.04	450	27.8	13.1	4.59
152	7.05	600	35.9	17.1	5.79
153	7.05	800	47.8	22.5	7.42
140	46.0	150	10.5	7.73	0.88
145	45.8	300	20.7	14.2	2.10
151	45.9	600	39.7	28.6	4.23
123	79.7	150	9.93	9.1	0.9
137	79.6	300	22.1	16.8	1.66
138	79.7	300	22.7	17.6	1.75

TABLE II. Reaction products at various times and pressures. High light intensity.

Expt. No.	$P_{B_2H_6}$ (cm)	Irradiation time (sec)	Products (μmoles) H_2	B_4H_{10}	B_5H_{11}
246	0.076	12.5	0.23	0.03	0.02
253	0.078	50	1.09	0.08	0.12
245	0.089	80	1.85	0.15	0.28
218	0.254	40	2.42	0.23	0.51
217	0.245	80	4.64	0.48	0.97
216	0.249	200	13.1	1.16	2.01
229	1.28	40	8.63	1.92	1.87
225	1.30	90	19.2	4.47	4.09
105	7.03	50	21.0	9.14	3.65
104	7.05	125	49.8	22.5	8.66
156	7.05	125	49.4	22.4	8.29
57	45.8	20	8.39	6.05	1.51
66	45.9	50	20.3	13.7	3.00
60	45.8	80	31.7	19.6	3.79
61	45.8	125	51.1	32.1	7.21
103	45.8	125	49.6	33.1	6.15
132	45.9	125	50.1	32.6	6.44
133	79.7	50	20.8	14.3	2.21
131	79.7	125	48.2	33.6	5.22

luminated. It was 4°C and independent of the pressure over the pressure range of interest.[13] The form of the temperature profile derived from the heat-flow equation in cylindrical coordinates is given by

$$T(r) = T_0 \ln(r_2/r)/\ln(r_2/r_0),$$

where T_0 is the temperature at the incident face, i.e., at the quartz jacket, and r_0 and r_2 denote the inner and outer radii, respectively, of the cylindrical reaction vessel. At r_2 the temperature is assumed to be 0°C. The average temperature, defined and measured as described above, essentially equals $\int T(r)2\pi r dr/\int 2\pi r dr$, for small gradients.[13] Substituting the above equation into this expression, T_0 was determined (r_2 and r_0 are known) to be 13°C. From the equation for $T(r)$, it can also be computed that 75% of the gas had a temperature between 0° and 6°C.

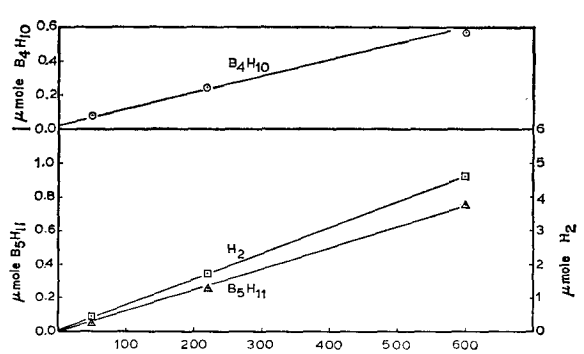

FIG. 2. Diborane photolysis. Plot of products vs irradiation time for a diborane pressure of 0.25 cm and low light intensity.

Actinometry

The conclusion that the 1849-Å line of the mercury lamp was responsible for the diborane photolysis was based on the facts that diborane absorbs strongly[11] near 1849 Å but is quite transparent above 2200 Å, and that on use of a 0.2M acetic acid filter (opaque to 1849 Å but transparent to 2537 Å) no photolysis was observed.

To determine the intensity of this 1849-Å line, purified ammonia at an atmospheric pressure was used as the actinometer, a useful one for measurement of the relative intensities.[15] A measurement of the absolute

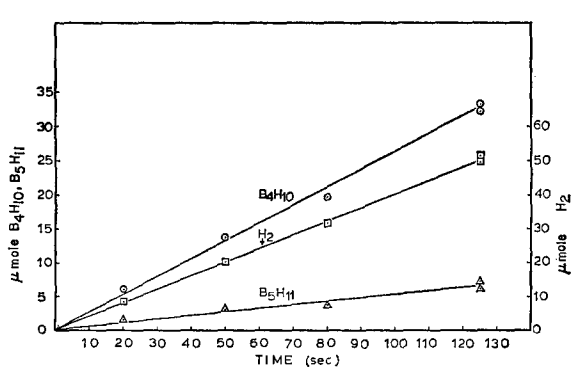

FIG. 3. Diborane photolysis. Plot of products vs irradiation time for a diborane pressure of 46 cm and high light intensity.

[15] The ratio of the products of static photolysis is $3H_2$ to 1 N_2, and the measurement of the noncondensables is simple. Ammonia at 1 atm absorbs 1849 Å strongly and is transparent to 2537 Å, and its quantum yield at 1 atm is essentially independent of intensity [cf. W. A. Noyes and P. A. Leighton, *Photochemistry of Gases* (Reinhold Publishing Corporation, New York, 1941), pp. 374–5].

TABLE III. Formation rates at various pressures. Low light intensity.

$P_{B_2H_6}$ (cm)	R_{H_2}	$R_{B_4H_{10}}$	$R_{B_5H_{11}}$ (μmoles/100 sec)	$R_{(-B_2H_2-)}$[a]	$-R_{B_2H_6}$[a]	$2R_{B_4H_{10}}+R_{(-B_2H_2-)}$
0.080	0.35	0.026	0.032	0.13	0.26	0.18
0.250	0.76	0.097	0.123	0.21_5	0.72	0.41
1.30	3.10	0.76	0.55	0.60	3.50	2.12
7.00	6.08	2.81	1.00	0.68	8.8	6.30
46.0	6.75	4.75	0.74	0.3	11.6	9.8
80.0	7.24	5.83	0.57	0.1	13.2	11.8

[a] Calculated.

intensity with it is uncertain, because the quantum yield depends somewhat upon cell geometry[16] and because of lack of data below 2100 Å.

Ammonia was irradiated at 1 atm. using the same irradiation procedure as in the diborane photolysis. The total amounts of noncondensables were 10.6 and 24.2 μmoles after 300 and 750 sec at "low" (i.e. H_2O-filtered) lamp intensity, and were 13.8 and 30.6 after 60 and 150 sec at "high" intensity.

From the slopes of the two lines, the ratio of the two rates and hence the ratio of the two intensities is 6.4. From the absolute rate it follows also that if the quantum yield of NH_3 photolysis at 1849 Å equalled its value at about 2100 Å, 0.16,[17] the (high) lamp intensity of the 1849-Å line transmitted into the cell would be about 0.64×10^{-6} einsteins/sec.

Rates of Formation

The products were measured for various reaction times, diborane pressures, and light intensities. The H_2 and B_4H_{10} values were corrected for "blanks."

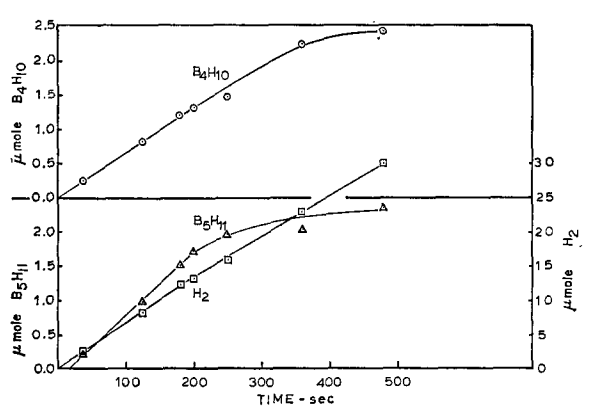

FIG. 4. Diborane photolysis. Plot of products vs irradiation time for an extended irradiation time, using a diborane pressure of 0.25 cm and high light intensity.

[16] E. O. Wiig, J. Am. Chem. Soc. **59**, 827 (1937).

[17] This value is the average of three reported values: 0.18 [E. O. Wiig, J. Am. Chem. Soc. **57**, 1559 (1935)], 0.16,[16] and 0.14 [R. A. Ogg, Jr., J. Am. Chem. Soc. **556**, 318 (1934)]. These were obtained using 1 atm of NH_3 at room temperature but in different reaction cells.

These blanks were determined by measuring the products when using either a 0.2*M* or 7*M* acetic acid solution as a filter in the photolysis, since the active 1849-Å line is thus completely removed. The maximum correction for H_2 was about -5%. No correction was necessary for B_4H_{10} at pressures of 7 cm or less, while at greater pressures the maximum correction was about -5%. No correction was necessary for B_5H_{11} at any pressure. The corrected values are presented in Tables I and II. In some earlier experiments made before the extensive precautions outlined in the beginning of this paper were taken, the blanks for B_4H_{10} and B_5H_{11} were as high as 50%.

Typical plots of amount of product vs irradiation times are given in Figs. 2 and 3. Two characteristics of the product vs time data are their linearity and, in 80% of the plots, their intersection of the origin. These results establish the absence of any induction period and any secondary reactions. Early experiments did show apparent induction effects, but with extensive conditioning of the reaction cell, the **U** traps, the Toepler pump, and the gas buret these effects were almost completely eliminated. Early experiments, such as that depicted by Fig. 4, showed that after somewhat longer reaction times the photolysis rate decreased markedly from its initial value.

Rates calculated from the slopes of the straight lines are presented in Tables III and IV. A detailed discussion of the random and systematic errors are given elsewhere,[13] where it is shown that the average deviation for the rates of formation of the three products is about $\pm10\%$.

Reaction Orders with Respect to Diborane Pressure and I_0

Log–log plots of rates vs pressure are shown in Figs. 5 and 6 for both light intensities. All plots begin to decrease in slope at about 4 cm. The pressure range (0.08 to 80 cm) is very large, and presumably at the low pressures the absorbed intensity is proportional to the pressure while at the high pressures, greater than about 10 cm, there is total absorption. This remark is supported by the linearity of the B_4H_{10} and H_2 curves

TABLE IV. Formation rates at various pressures. High light intensity.

$P_{B_2H_6}$ (cm)	R_{H_2}	$R_{B_4H_{10}}$	$R_{B_5H_{11}}$ (μmoles/100 sec)	$R_{(-B_2H_2-)}$[a]	$-R_{B_2H_6}$[a]	$2R_{B_4H_{10}}+R_{(-B_2H_2-)}$
0.080	2.12	0.17	0.34	0.63	1.83	0.97
0.250	5.88	0.59	1.22	1.40	5.64	2.58
1.30	21.7	4.94	4.61	3.9	25.4	13.8
7.00	40.7	17.8	6.80	4.8	57.3	40.4
46.0	40.2	26.4	5.35	1.6	67.8	5.4
80.0	39.2	27.2	4.02	1.8	66.4	5.6

[a] Calculated.

in Figs. 5 and 6 at low pressures and by calculations on the approximate absorption of diborane.[18]

The slopes of the log–log plots for the low-pressure data are given in Table V. The corresponding slopes for the high-pressure region could not adequately be made since experimental hazards limited the range of high-pressure measurements. Log–log plots of the rates vs incident light intensity I_0 have slopes (i.e. reaction orders with respect to I_0) given in Table VI.

Diborane Photolysis with Initial Hydrogen

The following reaction has been observed to occur at elevated temperatures.[19]

$$2H_2+2B_5H_{11}\rightarrow 2B_4H_{10}+B_2H_6.$$

The *linear* B_5H_{11} vs time plots obtained from Table I indicated that this reaction was unimportant under the present conditions, for otherwise convex plots would be obtained. In order to establish this fact more definitely, some diborane was photolyzed with a large amount of hydrogen present initially. The results obtained under typical conditions (a diborane pressure of 1.28 cm and a reaction time of 90 sec at the maximum lamp intensity) are as follows: In the presence and absence of 73 initially added μmoles H_2, the B_4H_{10} formation was 4.20 and 4.47 μmoles, respectively, and the B_5H_{11} was 4.16 and 4.09 μmoles. The H_2 formed in the absence of initially added H_2 was also measured and found to be 19 μmoles. Evidently, the addition of excess hydrogen did not affect the products.

TABLE V. Over-all reaction orders with respect to pressure at high and low intensities.[a]

Light intensity[a]	Order with respect to pressure[b] for following products: H_2	B_4H_{10}	B_5H_{11}	$(-B_2H_2-)$	B_2H_6	$2B_4H_{10}+(-B_2H_2-)$
High	0.7_9	1.2_1	0.9	0.6_2	0.9_4	0.9_5
Low	0.7_9	1.2_0	1.0	0.5_5	0.9_4	0.9

[a] The ratio of intensities is 6.4 from data at diborane pressures of 0.08, 0.25, and 1.30 cm.

[b] If R_i is rate of formation of product i, and n_i its order, then $R_i=k_iP_{B_2H_6}{}^{n_i}$.

[18] Figures 5 or 6 can be used to deduce the absorption coefficient of diborane, k.[13] Treating the reaction system as one of cylindrical symmetry, neglecting end effects, it can be shown that $I_a/I_0=(1-e^{-k(r_2-r_0)p})$ where $r_0=1.5$ cm, $r_2=5.2$ cm, and p is the diborane pressure (in cm). This equation may be fitted to the $R_{B_2H_6}$ vs p plot since $R_{B_2H_6}$ is first order in absorbed intensity (Tables V and VI). An excellent fit to the data of Fig. 6 (neglecting the slight increase at any high pressures) is obtained by the equation[13] $R_{B_2H_6}$ (μmole/100 sec) $=10.4\ (1-e^{-0.132p})$, whence $k=0.08$ cm^{-2}. This value is about 6.5-fold greater than a literature value,[11] which was stated to be an order of magnitude estimate because of absence of intensity markings.

[19] A. B. Burg and H. I. Schlesinger, J. Am. Chem. Soc. **55**, 4009 (1933).

MECHANISM

General

Since both B_4H_{10} and B_5H_{11} product vs time curves are linear, these two products are not formed one from the other under our conditions. Also, as the experiments show, H_2 is not a reactant in any of the elementary reactions.

It will be recalled that B_5H_{11} is formed in the thermal decomposition, B_4H_{10} in the Hg-photosensitized decomposition, and that BH_3 has been invoked to explain the former and B_2H_5 to explain the latter. Both B_5H_{11} and B_4H_{10} are formed in the photolysis. Partly for economy of postulates and partly because the consequences are consistent with the data, BH_3 and B_2H_5 will be used,

TABLE VI. Over-all reaction orders with respect to incident light intensity at various pressures.

$P_{B_2H_6}$ (cm)	Order[a] with respect to I_0 for the following products: H_2	B_4H_{10}	B_5H_{11}	$(-B_2H_2-)$	B_2H_6	$2B_4H_{10}+(-B_2H_2-)$
0.080	0.9_7	1.0_1	1.3	0.8_5	1.0_5	0.9_1
0.250	1.1_0	0.9_7	1.2_4	1.0_1	1.1_1	0.9_9
1.30	1.0_4	1.0_1	1.1_5	1.0_1	1.0_7	1.0_1
7.00	1.0_2	1.0_0	1.0_3	1.0_5	1.0_1	1.0_2
46.0	0.9_6	0.9_2	1.0_7	...	0.9_5	...
80.0	0.9_1	0.8_3	1.0_5	...	0.8_7	...

[a] If R_i is rate of formation of product i, and m_i its order, $R_i=k_iI_0{}^{m_i}$.

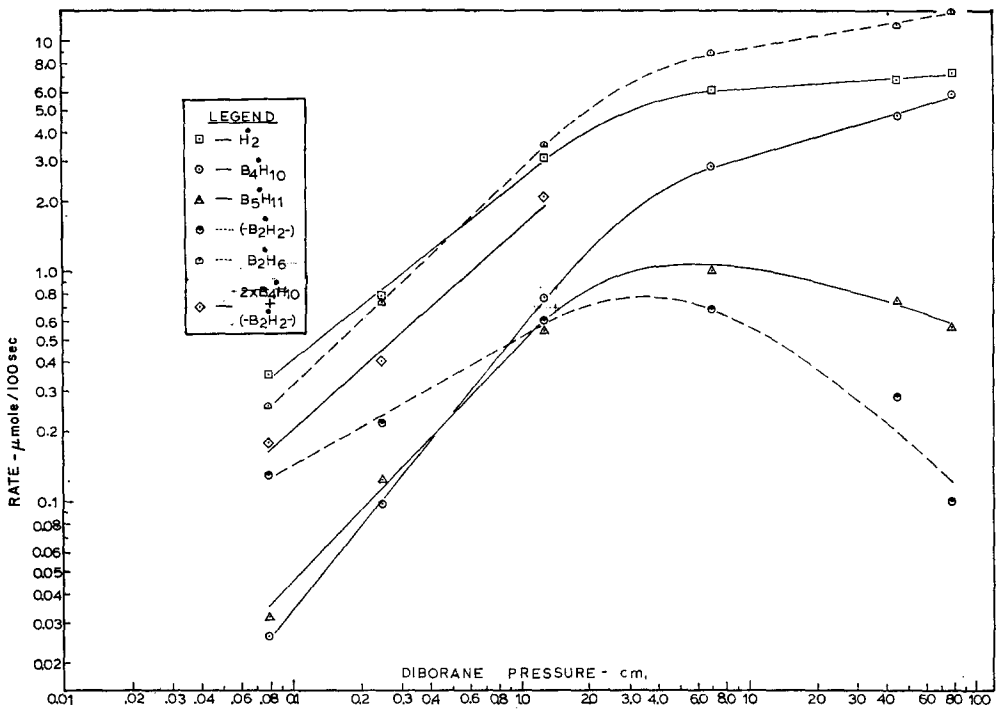

FIG. 5. Log–log plot of formation rates vs diborane pressures at high light intensity.

respectively, to interpret the formation of B_5H_{11} and B_4H_{10}. Elementary steps closely related to those invoked in the earlier studies will be used. However, it should be emphasized that this mechanism is a provisional one, because of the experimental problems described earlier.

B_5H_{11} Mechanism

At high pressures, Figs. 5 and 6 demonstrate, the B_5H_{11} rate decreases with increasing pressure. Accordingly, the primary photoexcitation of B_2H_6 will be

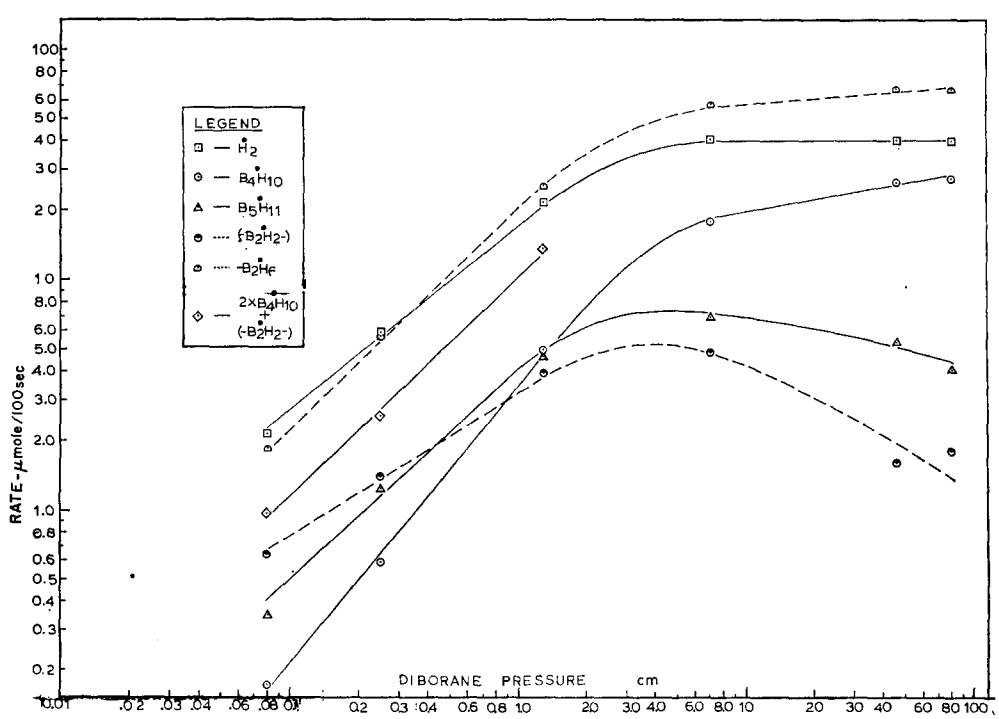

FIG. 6. Log–log plot of formation rates vs diborane pressure at low light intensity.

TABLE VII. Ratio of rates of formation of polymer and B_4H_{10} at various pressures and intensities.

$P_{B_2H_6}$ (cm)	$R_{(-B_2H_2-)}/R_{B_4H_{10}}$ High intensity	Low intensity
0.080	3.7	5.0
0.250	2.4	2.2
1.30	0.79	0.79
7.00	0.27	0.24

assumed to be followed by a deactivation which is competitive with a dissociation step. To account for the observed first-order dependence of B_5H_{11} upon I_a, a single fate will be assumed for BH_3 and for the subsequent intermediates. We then have:

$$B_2H_6+h\nu\rightarrow B_2H_6^*\xrightarrow{k_2}2BH_3 \qquad (I)$$

$$B_2H_6^*\xrightarrow[k_5]{+M}B_2H_6+M,$$

$$BH_3+B_2H_6\xrightarrow{k_3}B_3H_7+H_2,$$

$$B_3H_7+B_2H_6\xrightarrow{k_4}B_5H_{11}+H_2,$$

where M is the third body. The assumed absence of recombination of BH_3's in this photochemical system is discussed later.

Application of the steady-state hypothesis yields

$$R_{B_5H_{11}}=2\phi_1 I_a\alpha, \qquad (1)$$

where ϕ_1 is the primary quantum yield of step (I) and where α, a deactivation factor, is given by

$$\alpha=(1+k_5M/k_2)^{-1}. \qquad (2)$$

At sufficiently low pressures, α equals unity and I_a is proportional to pressure, so that in that pressure region the order of the reaction with respect to diborane pressure at constant I_0 and the order with respect to I_0 should each be unity. According to Tables V and VI, these orders are 1.0 and 1.2, respectively, in approximate agreement with this mechanism.

Due to the high reactivity of B_5H_{11}, its rate is subject to a greater uncertainty at low diborane pressures, as is evidenced by the observed sensitivity of this rate to conditioning procedures.[13] It cannot be definitely stated at this time whether the disagreement of 0.2 order in I_0 is due to experimental difficulties or to deficiency in mechanism.

In the high-pressure region, the reaction order with respect to I_0 is 1.0 (Table VI), as it should be according to Eq. 1. Moreover, the dependence of upon diborane pressure in Eq. 2 accounts for the falloff in rate above 7 cm (Figs. 5 and 6). The data are not sufficiently extensive to test the linearity of a plot of 1/rate vs pressure in this region, a linearity expected on the basis of Eqs. 1 and 2. However, the half-life of $B_2H_6^*$ calculated from such a plot is of the order of 10^{-10} sec, if one assumes a unit efficiency for the collisional deactivation step.

B_4H_{10} and Polymer $(-B_2H_2-)$ Mechanism

As comparison with the data will later show, it will be useful to assume that B_4H_{10} and polymer arise competitively from the same radical B_2H_5. The first-order dependence of both products upon I_0 (Table VI) implies that all elementary steps are of the same total order with respect to the short-lived species. The fractional diborane pressure orders imply that the dependence of the elementary steps upon diborane pressures is different. A mechanism consistent with these data is

$$B_2H_6+h\nu\longrightarrow B_2H_5+H, \qquad (II)$$

$$B_2H_5+H\xrightarrow{k_6}\cdots\longrightarrow(-B_2H_2-)+2H_2,$$

$$2B_2H_5\xrightarrow{k_7}B_4H_{10},$$

$$2H\xrightarrow{k_8}H_2.$$

The fourth and perhaps the third steps involve three-body restrictions, so that k_8 and possibly k_7 should be pressure dependent, increasing with increasing pressure. The second step may involve diffusion of the radicals to the walls, so k_6 could decrease with increasing pressure.

Applying the steady-state hypothesis, one obtains

$$R_{B_4H_{10}}=\phi_2 I_a/[k_6/(k_7k_8)^{\frac{1}{2}}+2], \qquad (3)$$

$$R_{(-B_2H_2-)}=[k_6/(k_7k_8)^{\frac{1}{2}}]\phi_2 I_a/[k_6/(k_7k_8)^{\frac{1}{2}}+2], \qquad (4)$$

where ϕ_2 is the primary quantum yield of step (II).

Both these equations agree with the observed first-order dependence upon I_0 of Table VI. The more complex dependence upon diborane pressure at constant I_0 can be tested in several ways. Since there are two reaction products, there are only two independent equations for the rates. Instead of testing the rather complex individual equations (the k's may be pressure dependent), it is considerably more convenient to test two related equations, one for the sum of the rates, and the other for their ratio. From the above equations for

B_4H_{10} and polymer, the following equations obtain:

$$(2R_{B_4H_{10}}+R_{(-B_2H_2-)})/I_a=\phi_2,$$
$$R_{(-B_2H_2-)}/R_{B_4H_{10}}=k_6/(k_7k_8)^{\frac{1}{2}}. \quad (5)$$

Thus, at low pressures, the order of $2B_4H_{10}+(-B_2H_2-)$ with respect to pressure should be unity, a result in agreement with the data in the last column of Table V. The expected decrease of $R_{(-B_2H_2-)}/R_{B_4H_{10}}$ with pressure, because of an anticipated increase of k_7k_8 (and possible decrease of k_6) is in qualitative agreement with the results of Table VII. The latter even suggest that k_8 is directly proportional to pressure. Further studies involving inert gases would elucidate the effect of the third-body dependence of k_7 and k_8.

At high pressures, the material balance is so good that any attempt to estimate the relatively negligible polymer from deviations from this material balance becomes subject to large errors. According to the low-pressure data in Table VII [or Eq. (5)] polymer should indeed become negligible at high pressures, unless new mechanisms for its formation begin to contribute.

At sufficiently high pressures, the mechanism outlined earlier for B_4H_{10} formation would lead to a constant quantum yield $\frac{1}{2}\phi_2$ since one then has $k_6/(k_7k_8)^{\frac{1}{2}}\ll 2$ [cf. comparison of Table VII and Eq. (5)]. There appears, however, to be a slight rise in B_4H_{10} rate (and therefore in its quantum yield, in the pressure region of complete light absorption). Should this increase be verified, it would not be unreasonable to expect the reaction

$$H+B_2H_6\rightarrow H_2+B_2H_5,$$

to occur at high diborane pressures.

Remarks on Quantum Yields and on BH_3 Recombination

The approximate values for several quantum yields can be obtained from the data for the high-pressure region of complete light absorption. If $1/R_{B_5H_{11}}$ is plotted vs $P_{B_2H_6}$ for pressures greater than 7 cm, one can calculate from the average intercept a primary quantum yield, $\phi_1=0.06$ [cf. Eq. (1)]. Second, one can calculate from $R_{B_4H_{10}}/I_0$ an average $\phi_2=0.5$, since the ratio $k_6/(k_7k_8)^{\frac{1}{2}}$ becomes much less than 2 [cf. Eq. (3) and Table VII]. Finally, since the over-all diborane quantum yield $\phi_{B_2H_6}$ equals $2\phi_2+5\phi_1$, $\phi_{B_2H_6}=1.3$.[20]

Some discussion of the recombination step of BH_3's here and in the thermal studies is pertinent. It will be recalled that over-all fractional orders characterize the thermal data for B_5H_{11} formation, and establish the importance of the BH_3 recombination. However, in the present photochemical data unit orders were obtained, so recombination is minor. This apparent difference may be due to the photochemically produced BH_3 groups possessing considerably greater energy than the thermal ones, inasmuch as the energy of the 1849-Å line 155 kcal mole^{-1} is very much in excess of that needed to dissociate B_2H_6, which appears[21] to be about 30 kcal mole^{-1}. This excess energy could facilitate the subsequent attack of BH_3 upon the B_2H_6 molecule.

As an alternative explanation for the above kinetic difference, it is possible that the BH_3 concentration in the photolysis is much lower than in the thermal reaction—so low that the magnitude of the recombination step $k_r(BH_3)^2$ is much less than the rate of attack of BH_3 upon B_2H_6, $k_3(BH_3)(B_2H_6)$. It follows from the condition for such behavior that $k_rR_{B_5H_{10}}/k_3^2(B_2H_6)^2$ would be much less than unity in the photolysis reaction, while in the thermal reaction the ratio would be much greater than unity. Since the $R_{B_5H_{11}}$ and (B_2H_6) are comparable in both reactions,[22] a positive activation energy for k_r/k_3^2 is necessary to account for the above difference in inequalities and one would conclude that BH_3 recombination has an appreciable activation energy. Using the analytical techniques described in this paper, it should be possible to extend the thermal studies to lower temperatures and thus measure the activation energy of k_r/k_3^2, if the alternative explanation is valid.

[20] As noted previously, when better quantum yields are obtained for the ammonia photolysis at 1849 Å, these ϕ's will be changed accordingly.

With these values of ϕ_1 and ϕ_2, $\phi_{B_4H_{10}}$ and $\phi_{B_2H_2}$ at any pressure may be approximately obtained from Eqs. (3), (4), and (5) and Table VII. For example, $\phi_{B_4H_{10}}=\phi_2/(2+R_{B_2H_2}/R_{B_4H_{10}})$. $\phi_{B_5H_{11}}$ at any pressure below 7 cm is $2\phi_1$, approximately, while at any higher pressure p it is roughly $R_{B_5H_{11}}$ (p cm)$/R_{B_5H_{11}}$ (7 cm).

[21] S. H. Bauer, J. Am. Chem. Soc. **78**, 5775 (1956).

[22] In reference 3, $(B_2H_6)=76$ cm and $R_{B_5H_{11}}=19$ μmoles/100 sec at 112°C, while in this photolysis at high light intensity, $(B_2H_6)=80$ cm and $R_{B_5H_{11}}=4.0$ μmoles/100 sec at 4°C.